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Composition of Size-Fractionated Aerosol in Charleston, West Virginia

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16. ABSTRACT

Atmospheric aerosols were collected during a 21 day period in late summer of 1976 in Charleston, West Virginia, using five dichotomous virtual impactor samplers simultaneously. The resulting coarse and fine aerosol were analyzed with a variety of physical and chemical methods: gravimetrically for total mass; by XRF for elements heavier than Mg; by proton induced gamma-ray emission for C, N and S; by ion chromatography for sulfate, nitrate and Na; and by ion selective electrode for ammonia.

It was inferred that sulfur and nitrogen in the fine fraction were almost entirely in the form of ammonium sulfate, accounting for 41% of the total fine particle mass. Carbon was a large component of both fine and coarse particle mass, constituting 16% and 12%, respectively.

Factor analysis of the data indicated that four factors were sufficient to satisfactorily represent the variance of 26 measured parameters. The factors are characteristic of crustal material, ammonium sulfate, automotive emissions, and an unidentified anthropogenic source or set of sources.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution * Aerosols * Particle size distribution * Chemical analysis	Charleston, WV	13B 07D

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COMPOSITION OF SIZE-FRACTIONATED AEROSOL IN CHARLESTON, WEST VIRGINIA

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Abstract – Atmospheric aerosols were collected for 21 days in summer 1976 at Charleston, West Virginia, using five dichotomous virtual impactor samplers simultaneously. The samplers fractionated the aerosol into two aerodynamic size ranges, a fine ($<3.5\ \mu m$) and a coarse ($>3.5\ \mu m$) fraction. Physical and chemical composition of the aerosol in each size range was measured by filter weighing (total mass), proton induced gamma-ray analysis (carbon, nitrogen, and sulfur), X-ray fluorescence (elements heavier than magnesium), ion chromatography (sulfate, nitrate and sodium), and ion selective electrode (ammonium). Fine particle sulfur was found to be in the form of sulfate. Less than 1% of fine nitrogen was in the form of nitrate; more than 99% was present as ammonium ion. The high correlation between fine sulfur and nitrogen ($r = 0.92$) and fine sulfate and ammonium ($r = 0.98$) and the presence of sulfate and ammonium in the stoichiometric ratio for ammonium sulfate strongly suggest that ammonium sulfate was the main chemical form of fine sulfur and nitrogen. A detailed mass composition was determined for each particle size range, identifying 69 and 60% of the fine and coarse mass, respectively. Ammonium sulfate was the largest single chemical component (41%) of the fine aerosol mass. Carbon was also a large component of both fine and coarse particle mass constituting 16 and 12% respectively. Factor analysis indicated that four factors were sufficient to satisfactorily represent the variance of 26 measured parameters. The factors are characteristic of crustal material, ammonium sulfate, automotive emissions, and an unidentified anthropogenic source or set of sources.

INTRODUCTION

Accounting for the *chemical*, or at least the *elemental*, composition of aerosols has been a long term objective in atmospheric aerosol investigations. Knowledge of the elemental composition of aerosol can point to likely compounds, guide future chemical analyses, and can set upper limits for the concentrations of any possible compounds containing those elements. Elemental data can also lead to a remarkably detailed determination of pollutant sources. The value of elemental and chemical composition data is significantly enhanced when accompanied by aerosol particle size information since the size affects the respirability of the aerosol, governs its impact on visibility reduction, determines its potential for long range transport and indicates possible sources.

The desire for information on chemical speciation as a function of particle size must be tempered however by the need for sufficient quantity of aerosol for chemical analysis. The dichotomous virtual impactor (Dzubay *et al.*, 1977) provides a useful compromise in this circumstance. This sampler fractionates aerosol into two aerodynamic size ranges yielding "fine" and "coarse" samples, which approximately correspond to respirable and non-respirable aerosol, respectively. Sampling intervals on the order of one day or less normally yield fine and coarse aerosol samples of sufficient quantity to perform a variety of elemental, chemical and gravimetric analyses.

In this paper we report the results of a sampling study using several dichotomous samplers, performed at one site in Charleston, West Virginia, during the late summer of 1976. Charleston is at the eastern end of a 30 km long, heavily industrialized area along the Kanawha River, in a narrow valley (1–2 km width) formed by hills of about 200 m in height. The area population is approx 200,000, about half of which resides in Charleston. The air quality in this area has undergone extensive investigation in the past (Kanawha Valley Air Pollution Study, 1970).

The use of multiple samplers operating at a single site, allowed (1) a comparison of the consistency of results obtained with samplers thought to be equivalent, and (2) the collection of a set of replicate samples for several physical and chemical analyses. The first objective provided a degree of quality assessment which is frequently absent in such studies. The second objective permitted a more thorough elemental characterization of the aerosol than has usually been achieved.

This work includes the analysis of carbon and nitrogen among the measured elements. Even though these elements are expected to be major constituents of atmospheric aerosol they have not often been measured in past studies. Their inclusion has made possible a detailed mass balance in the two particle size ranges. Finally, sources of the measured aerosol were examined by several statistical techniques including

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correlation coefficients, factor analysis and enrichment factors.

SAMPLING

Aerosol sampling was performed continuously during a 21 day interval from 25 August to 14 September, 1976, on the roof of the five story Federal Building in the city center of Charleston, West Virginia. Five manual dichotomous virtual impactor samplers (Environmental Research Corp., St. Paul, MN 55112) were operated simultaneously at the site for 24 h sampling periods beginning at 1100 EDT. All samplers had a 14 l min^{-1} inlet flow rate, partitioned into a fine particle flow rate of 13.6 l min^{-1} and a coarse particle flow rate of 0.4 l min^{-1}, and all had a coarse-fine aerosol cut point of 3.5 μm aerodynamic dia. Three samplers used Sierra Model 250 Constant Mass Flow Controllers (Sierra Instruments, Carmel Valley, CA 93924) and two used rotameters to control the fine particle flow rate. The coarse particle flow was set by rotameters for all samplers. The performance of all five was monitored throughout the study by measuring the total flow immediately before and after each 24 h sampling period with a dry test meter. The average values of the daily absolute changes in flow were 2.1 and 3.0% for the samplers equipped with mass flow controllers and rotameters, respectively.

Samplers were equipped with either Fluoropore FALP 1 μm pore size filters (Millipore Corp., Bedford, MA 01730) or Tissuquartz 2500 QAO filters (Pallflex Products Corp., Putnam, CT 06260). Fluoropore membrane filter was suitable for gravimetric, X-ray fluorescence and wet chemical analyses but the carbon analysis required a filter having no more than trace amounts of carbon. A quartz fiber filter was chosen over glass fiber because of the generally superior characteristics of the former regarding artifact sulfate (Coutant, 1977) and nitrate (Spicer *et al.*, 1978) formation. To further decrease the importance of blank subtraction in the carbon analyses, the surface density of collected carbon was enhanced by reducing the diameter of the aerosol deposit to 12.7 mm compared with 29.0 mm used with the Fluoropore filters. This concentration step was accomplished by mounting the filters in special holders having the smaller exposure area, and by inserting before each filter an aluminum cylinder with a tapered bore to guide the aerosol into the smaller area.

For all five samplers the flow rate at the inlet of the virtual impactor was 14 l min^{-1}. In four of the five this was accomplished by isokinetic sampling from a total flow rate of 200 l min^{-1} into the sampler head. Wind tunnel measurements by Wedding *et al.* (1977) indicate that the sampling effectiveness of this system is characterized by a 50% efficiency for particles near 20 μm aerodynamic dia. Below about 5 μm the sampling effectiveness is virtually 100% (Dzubay *et al.*, 1977). The fifth sampler had an inlet head system substantially different from the other four, utilizing 14 instead of 200 l min^{-1} as the total inlet flow. In spite of this, intercomparisons of sample analyses from all five samplers showed that all samplers could be regarded as essentially identical for this study.

ANALYSIS

1. *Gravimetric*

The mass of aerosol collected on each Fluoropore filter was measured gravimetrically to a precision of 10 μg using an electrobalance in a 50% average relative humidity atmosphere. No mass measurement was carried out with Tissuquartz, because this filter medium is extremely hygroscopic. Each pair of fine and coarse mass measurements was used to calculate the corresponding atmospheric mass concentrations ($\mu g\ m^{-3}$) in the two size ranges by means of equations given by Dzubay *et al.* (1977). Analogous equations were used to calculate atmospheric elemental and ionic concentrations from the measurements described below.

2. *Elemental*

Proton Induced Gamma-Ray Analysis (Macias *et al.*, 1978) was applied to the Tissuquartz filters to obtain non-destructive measurements of total carbon, nitrogen and sulfur. The Fluoropore filters were non-destructively analyzed with an energy dispersive pulsed X-ray fluorescence (XRF) system (Jaklevic *et al.*, 1976) for elements heavier than magnesium, using the data reduction procedures of Stevens *et al.* (1978). Three commercial instruments employing combustion principles were used for carbon and nitrogen analyses of Tissuquartz filters: Model 240 Elemental Analyzer (Perkin-Elmer Corp., Norwalk, CT 06856), Dohrmann DC-50 Carbon Analyzer (Envirotech Corp., Santa Clara, CA 95050), and Model 734-100 Low Carbon Analyzer (Leco Corp., St. Joseph, MI 49085). The procedures used in their operation have been given by Macias *et al.* (1978).

3. *Chemical*

The Fluoropore filters were ultrasonically extracted and subjected to two wet chemical procedures: (1) ion exchange chromatography to measure sulfate (SO_4^{2-}), nitrate (NO_3^-) and sodium (Na^+), and (2) ion selective electrode for ammonium (NH_4^+). Details of the extraction and analytical methods have been given by Stevens *et al.* (1978).

VALIDATION OF TECHNIQUES AND EQUIPMENT

1. *Intersampler comparison*

During the first 10 days aerosol samples were collected simultaneously from three samplers using Fluoropore filters. From the gravimetric and XRF analyses performed on these filters it was possible to investigate the agreement between the three nominally identical samplers regarding their characterization of the sampled aerosol. Table 1 gives this comparison in terms of the average % standard deviation σ_x for each element (or the total mass) x, with σ_x defined as

$$\sigma_x = \frac{1}{N} \sum_{k=1}^{N} \sqrt{(n-1)^{-1} \sum_{i=1}^{n} [(x_{ik} - \bar{x}_k)/\bar{x}_k]^2}. \quad (1)$$

In the equation, N = number of sampling periods (10), n = number of samplers (3), x_{ik} = concentration of element x measured by sampler i on day k, and $\bar{x}_k$ = average concentration for element x measured by all samplers on day k. As so defined, each σ_x is a measure of the average precision with which the corresponding atmospheric elemental concentration can be determined in one measurement performed on one sample taken with any of the three samplers.

Copper and zinc were not included in Table 1 because the coarse fraction concentrations measured

Table 1. Intersampler % standard deviations (σ) computed from Equation (1), using three samplers

Measured Parameter	Fine σ (%)	Coarse σ (%)
Mass	5	15
Al	‡	34
Si	19	18
S	9	32
Cl	62†	53*
K	18	17
Ca	21	20
Ti	‡	29
Mn	37†	40*
Fe	19	22
As	51†	‡
Se	21	‡
Br	6	20
Sr	29*	24
Pb	6	22
Average§	11	23

* 5–10% of measurements below decision limit.
† 20–40% of measurements below decision limit.
‡ More than 60% of measurements below decision limit.
§ Weighted by elemental abundances of Table 3, mass excluded.

for them by one of the three samplers were unrealistically high, by factors of about 100 and 20, respectively, relative to the averages of the other two samplers. Enhancement in the fine fraction was also observable but to a much smaller degree. Unfortunately, the suspect sampler was discarded prior to discovery of the problem so that a follow-up investigation was not possible. The origin was assumed to be debris from a malfunctioning pump motor within the sampler. Such an effect has been suggested before (Camp *et al.*, 1978).

Table 1 shows that total mass in the fine and coarse fraction is measured more precisely (5 and 15%, respectively) than any of the elemental constituents in a fraction. As expected, standard deviations within each size fraction generally increase with the number of measurement values below the XRF decision limit, as defined by Currie (1977). However if the tabulated standard deviations are weighted by elemental relative abundance and averaged, the fine and coarse averages are seen to be 11 and 23%, respectively. Thus although the uncertainties listed in Table 1 cover a wide range the more abundant elements are measured with acceptable precision. The results in Table 1 were used to select those elements measured accurately enough to justify their inclusion in subsequent analyses (correlation coefficient and factor analysis). Any fine or coarse component with an average standard deviation larger than 35% was arbitrarily excluded from further consideration.

2. *Intermethod comparisons*

The elements for which different analysis methods can be compared are carbon, nitrogen and sulfur. The results of the comparison, in which the gamma-ray method was regarded as the standard, are given in Table 2. The results are again expressed in terms of average % standard deviations, as defined in Equation (1), with $n = 2$ and N between 10 and 21. The conditions for a true intermethod comparison were best satisfied by the combustion methods (the Dohrmann and Perkin-Elmer instruments) since each Tissuquartz filter from the same set of filters measured with the (non-destructive) gamma-ray method was subsequently measured by one or the other (destructive) combustion method. The remaining method (XRF) used Fluoropore filters; the slightly worse results (14%) for this comparison may reflect the additional potential sources of variation related to the use of different samplers and different filter media.

Table 2. Average standard deviations (%)* between results from gamma-ray method and alternative methods (fine fraction samples only)

Element	Combustion Dohrmann DC-50	Combustion Perkin–Elmer 240	XRF
C	5	11	
N		12	
S			14

* Blank indicates measurement not possible.

The results in Table 2 are from the fine aerosol fraction only. For the coarse fraction, only carbon was present in sufficient quantity to permit a quantitative intermethod comparison. The results, however, were strikingly different than those for the fine fraction: the ratio of carbon found by combustion techniques to that determined by the gamma-ray method was only 0.66, averaged over measurements from 20 coarse samples. By comparison the corresponding ratio for the fine carbon fraction was 1.03, averaged over 25 samples, thus indicating essentially no systematic difference between methods. Macias *et al.* (1978) suggest the origin of the discrepancy is in sampling and/or handling problems rather than analytical differences, although some uncertainty remains.

RESULTS AND DISCUSSION

1. *Aerosol elemental concentration*

During the first two days (25–26 August) of the study, Charleston was on the periphery of a large scale hazy air mass hundreds of kilometers across, as seen in visibility contour maps (Husar *et al.*, 1976). The hazy air mass was located initially throughout the Ohio River and lower Mississippi River basins (23–24 August) then moved north and then east through New England and southeastern Canada. Most elements showed high concentrations during these two days, which undoubtedly was associated with the presence of this air mass.

Table 3 presents the average concentrations for all

Table 3. Average total mass and elemental composition in Charleston WV, during the period 25 August–14 September, 1976

Component	Fine ($\mu g\ m^{-3}$)	Coarse ($\mu g\ m^{-3}$)
Mass	33.4	27.1
C	5.2	3.2
N	3.3	0.46
Na	0.19*	0.034†
Al	0.074	1.1
Si	0.41	2.8
S	3.3	0.34
Cl	0.04	0.08
K	0.10	0.29
Ca	0.099	0.96
Ti	0.011	0.077
Mn	0.007	0.01
Fe	0.15	0.59
Cu	0.020	0.004
Zn	0.032	0.01
As	0.026	‡
Se	0.007	‡
Br	0.15	0.039
Sr	0.004	0.004
Pb	0.66	0.12

* Based on data from 4–14 September only.
† Based on data from 8, 12 and 14 September only.
‡ Below detection limit.

the elements measured during the study, separated into fine and coarse fractions. The average total aerosol mass (the sum of both size fractions) during the 21 day sampling period was 61 $\mu g\ m^{-3}$, while the maximum value for a single 24 h sampling period was 112 $\mu g\ m^{-3}$, measured during the first day. For comparison total suspended particulate (TSP) values measured by the West Virginia Air Pollution Control Board with a hi-volume sampler at the same site during 1976 were 85 $\mu g\ m^{-3}$ (third quarter average), 186 $\mu g\ m^{-3}$ (third quarter maximum), and 97 $\mu g\ m^{-3}$ (annual average). Total mass measurements made with dichotomous samplers are generally smaller than TSP results, primarily because of the larger sampling efficiency for larger particles of the hi-volume samplers (Stevens *et al.*, 1978).

Carbon is notably the only major element that is about equally distributed between the two size fractions, constituting 16 and 12% of the fine and coarse masses, respectively. These percentages are similar to those found in size-fractionated carbon measurements made in Columbus, Ohio and New York City (Miller *et al.*, 1973) and in St. Louis, Missouri and West Covina, California (Spicer, 1976). These results contrast with those from a smaller set of measurements made by Appel *et al.* (1976) at several Southern California sites, which showed (somewhat indirectly) no carbon in the coarse fraction.

2. *Chemical form of nitrogen and sulfur*

The results of SO_4^{2-}, NO_3^-, and NH_4^+ analyses are given Table 4, as ratios of the amount of the element in the specified chemical form to the total amount of that element. The ratios (and corresponding standard deviations) shown are averages over the full 21 day sampling duration. The total elemental values used in the ratios were taken from gamma-ray measurements of nitrogen, and XRF measurements of sulfur. The advantage of the latter was that the same filters subjected to (non-destructive) XRF analysis were subsequently used in the wet chemical analyses.

Table 4. Average ratios of sulfur and nitrogen in the forms of sulfate, ammonium and nitrate to the total amounts of sulfur and nitrogen (fine aerosol only)

Chemical form	Ratio
$(S)_{sulfate}/(S)_{total}$	1.01 ± 0.14
$(N)_{ammonium}/(N)_{total}$	1.08 ± 0.45
$(N)_{nitrate}/(N)_{total}$	0.007 ± 0.008

The $(S)_{sulfate}/(S)_{total}$ and $(N)_{ammonium}/(N)_{total}$ ratios are both unity within error, indicating that in this study the particulate sulfur and nitrogen in the fine fraction are in the ionic form of sulfate and ammonium, respectively, with the nitrate contribution being very small. Figure 1 shows the high degree of correlation between NH_4^+ and SO_4^{2-} measurements on each filter. The measured pairs cluster closely about the line corresponding to the theoretical relationship for $(NH_4)_2SO_4$, in agreement with previous results (Stevens *et al.*, 1978). We assume that this result accurately reflects the chemical form of the aerosol as it exists in the atmosphere prior to sampling. However because no precautions were taken to preserve sample acidity, and because the extent to which H_2SO_4 exists in the atmosphere is poorly known at present, the assumption must be treated with caution.

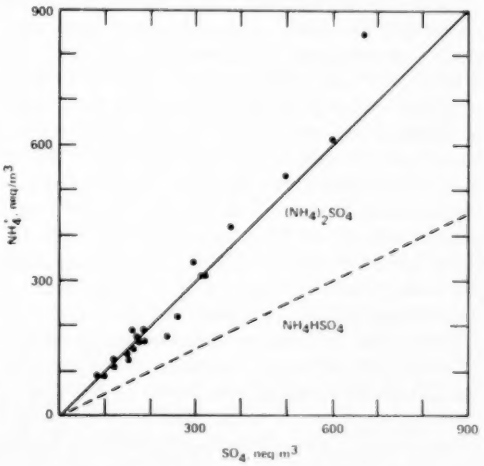

Fig. 1. Comparison of ammonium and sulfate analyses (in nanoequivalents m^{-3}) for fine aerosol samples from every sampling day. The lines indicate the ideal relationships expected for ammonium sulfate (solid line) and ammonium bisulfate (dashed).

The relationship between fine sulfur and sulfate shown in Table 4 has been previously demonstrated for several widely distributed sites in the U.S. (Stevens *et al.*, 1978). The observed dominance of fine nitrogen as ammonium over fine nitrogen as nitrate can also be inferred from previous measurements at Eastern and Central U.S. sites (Miller *et al.*, 1973; Spicer, 1976). In the same studies the ammonium form of nitrogen was dominant at one Southern California site, while at the other the amounts of the two forms of fine nitrogen were comparable. As in the present work those studies used neutral high purity quartz filters to minimize nitrate artifact formation.

3. *Mass balance*

By using the average elemental concentrations of Table 3 and the known or assumed chemical forms of the elements, a detailed aerosol mass balance can be determined for the two size fractions. The results are given in Fig. 2. As shown, 69 and 60% of the fine and coarse aerosol mass, respectively, can be accounted for by this procedure. Taken together, 65% of the total mass (coarse and fine) is accounted for. The assumptions used in the construction of Fig. 2, which extend beyond what has been experimentally established in this work, are: (1) nitrogen and sulfur in the coarse fraction exist in the form $(NH_4)_2SO_4$, (2) carbon occurs in the form $-CH_2-$, and (3) most of the metals exist as oxides. These are discussed in the following.

Measurements of NH_4^+, NO_3^- and SO_4^{2-} in the coarse fraction had large uncertainties, because of the relatively small amounts of nitrogen and sulfur present, leaving the ammonium sulfate assumption beyond experimental verification for the coarse fraction. If all nitrogen in the coarse fraction were in the form of NO_3^- instead of NH_4^+ as assumed, the percentage of coarse mass accounted for would increase from 60 to 65%. For the less extreme hypothesis that an amount of coarse NH_4^+ is present to stoichiometrically balance coarse SO_4^{2-} and the remaining coarse nitrogen is in the form of NO_3^-, the percentage of identified coarse mass would increase from 60 to 62%.

In general, ambient particulate carbon is expected to be present in organic compounds, in the elemental state as soot, and as carbonate (CO_3^{2-}). The work of Mueller *et al.* (1972) showed carbon as carbonate to be less than 5% of all TSP carbon in Pasadena. In the present work assumption of a carbonate form would be the most likely and would also have the largest impact for the case of calcium. Even in this case however the percentage of identified coarse mass would increase from 60 to only 62%, and leave the identified fine fraction percentage virtually unchanged. The question of organic versus soot forms of ambient particulate carbon is currently a matter of controversy (Novakov, 1978). In this circumstance the $-CH_2-$ assumption is somewhat arbitrary. However the choice of $-CH_2-$ instead of C has relatively little effect on the percentage of identified mass. There is likely to be some oxygen associated with organic carbon (for example organic acids), but this is expected to have a small effect on the mass balance and thus has been ignored.

The choice of oxides for the metallic elements reflects both the usual form of their occurrence in the earth's crust (Mason, 1966) as well as the common end result of combustion processes. An interesting example of the latter is the case of lead. The work of Ter Haar and Bayard (1971) and others has shown that the chemical form of particulate lead from automobiles is complex and dependent on the aerosol age. The fresh aerosol is dominated by lead halides such as PbBrCl, but the aged aerosol is composed largely of lead oxides and carbonates.

Overall, the assumptions used in constructing Fig. 2 lead to conservative estimates of the percentage of identified aerosol mass. At the same time the previous arguments show that the percentage of identified mass is surprisingly stable under reasonable changes in the assumptions.

4. *Role of water in unidentified mass*

Oxygen is the only element of expected importance not measured in this study, although it has been

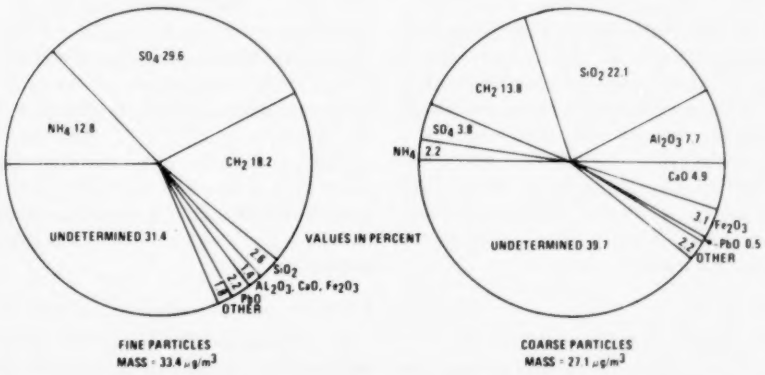

Fig. 2. Average percentage chemical composition of total fine and coarse aerosol mass. The category "other" includes Na, Cl, K, TiO_2, MnO_2, CuO, ZnO, As_2O_3, SeO_2 and Br.

partially included implicitly in the mass balance through the identification of sulfur with sulfate, and by the assumption that most of the metals exist as oxides. Water, however, is the most obvious oxygen containing compound not yet addressed in the study.

To gain some information on this question the following simple experiment was performed. Eight of the Fluoropore filters, half with fine aerosol deposit and half with coarse aerosol, were exposed for at least 24 h to a series of relative humidities between 0 and 95% in a desiccator containing a saturated solution of a salt chosen to produce the desired humidity. After each exposure the filters were weighed as quickly as possible on a microbalance. Figure 3 shows the result obtained for a representative fine and coarse filter, expressed as the ratio of the apparent aerosol mass at each humidity to the mass at zero humidity. The coarse filter aerosol mass is constant within experimental error, while the fine filter mass shows a large increase beyond about 70% relative humidity. The fine filter measurement at 95% relative humidity was qualitative only, since the mass was observed to decrease very rapidly upon removal of the filter from the desiccator. Four clean Fluoropore filters, serving as controls, showed no significant change in mass when compared at the two humidity extremes.

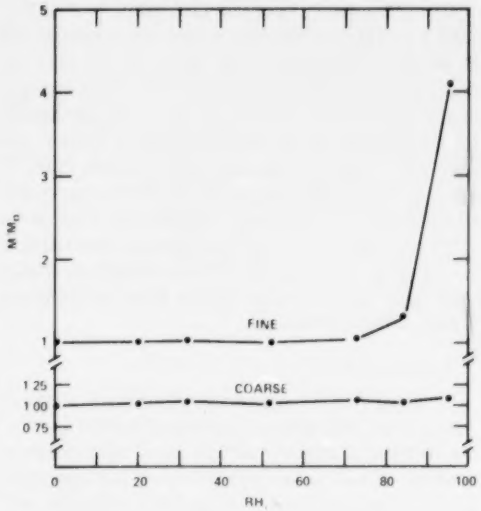

Fig. 3. Measured mass of fine and coarse aerosol, relative to mass at zero relative humidity, as a function of relative humidity.

These results can be explained by the behavior of ammonium sulfate which constitutes about 40% of the fine aerosol mass, but an order of magnitude smaller percentage of the coarse mass. The dramatic increase in mass experienced by pure ammonium sulfate at relative humidities greater than 72% is well documented (Macias and Husar, 1976; Lundgren *et al.*, 1976). Thus we speculate that the relative amounts of ammonium sulfate present on the fine and coarse filters is the dominant factor underlying the results of Fig. 3, with some modification from the remaining aerosol compounds. Extensive measurements of this relative humidity effect have been made by Winkler and Junge (1972), although no particular emphasis was given to the behavior of ammonium sulfate at that time. The results of Fig. 3 show that gravimetric measurements of collected aerosol mass can be made below 60% relative humidity, without a contribution from water absorbed by the collected aerosol. However no conclusions regarding the possible presence of water of hydration can be drawn from the preceding experiments. Water in this form is much more stably bound, and is not readily released when the humidity is decreased below the point at which the hydrate was formed. Preliminary results reported by Winkler and Junge (1972) suggest water of hydration represents 5–10% of aerosol mass. Future studies should quantitatively address this matter.

5. *Correlation analysis*

The matrix of linear correlation coefficients C_{ij} ($-1 \leqq C_{ij} \leqq +1$) for all elemental pairs which meet the 35% standard deviation criterion discussed above are given in Table 5. Based on the number of pairs (21) contributing to each coefficient, an entry whose absolute value exceeds 0.55 indicates a statistically significant ($\rho = 0.01$) relationship. The use of correlation coefficients allows a quantitative estimate of the similarity of the temporal variations of any two species. Highly correlated species may come from the same primary source or secondary transformation process, or the correlation may indicate the species are carried together in the same air mass.

Table 5 indicates high correlations between fine sulfur and fine nitrogen ($r = 0.92$) and between fine sulfur and fine mass ($r = 0.87$). The first correlation is consistent with all the previous evidence pointing to $(NH_4)_2SO_4$ as the chemical form of the fine sulfur and nitrogen measured in this study. This compound represents about 40% of the fine mass, which in turn explains the high correlation of fine sulfur and mass. The moderately high correlation of fine carbon with fine lead ($r = 0.80$) indicates that automotive vehicles are an important but not exclusive source of carbon. Fine carbon has a low correlation with fine sulfur ($r = 0.49$), shedding some doubt on the catalytic effect of carbon on particulate sulfate formation, as proposed by Novakov *et al.* (1974). Fine silicon shows a moderately high correlation with a number of elements such as fine K, Ca, Fe, Zn, Se and Sr. Coarse particle species with high mutual correlations include Si, K, Ca, Ti, Fe and Sr, all of which are found in soil and coal.

6. *Factor analysis and crustal enrichment*

Factor analysis (Harmon, 1967) was also used to deduce interrelationships between the measured elemental concentrations. This approach has been used rather successfully to analyze atmospheric aerosol

Table 5. Linear correlation coefficients*

	Mass-F	C-F	N-F	Si-F	S-F	K-F	Ca-F	Fe-F	Zn-F	Se-F	Br-F	Sr-F	Pb-F	Mass-C	C-C	N-C	Al-C	Si-C	S-C	K-C	Ca-C	Ti-C	Fe-C	Br-C	Sr-C	Pb-C
Mass-F	**1.00**																									
C-F	**0.56**	**1.00**																								
N-F	**0.79**	0.54	**1.00**																							
Si-F	0.47	**0.68**	0.35	**1.00**																						
S-F	**0.87**	0.49	**0.92**	0.34	**1.00**																					
K-F	0.52	**0.63**	0.37	**0.72**	0.33	**1.00**																				
Ca-F	**0.73**	**0.63**	**0.58**	**0.67**	**0.56**	**0.79**	**1.00**																			
Fe-F	**0.72**	**0.58**	0.36	**0.70**	0.47	**0.79**	**0.83**	**1.00**																		
Zn-F	0.17	0.47	0.23	**0.75**	0.16	**0.59**	0.42	0.37	**1.00**																	
Se-F	**0.57**	**0.66**	0.52	**0.75**	0.40	**0.68**	**0.76**	**0.55**	**0.65**	**1.00**																
Br-F	0.14	**0.64**	0.29	0.35	0.21	0.48	0.45	0.19	0.49	0.46	**1.00**															
Sr-F	0.14	**0.66**	0.30	**0.74**	0.14	0.49	0.34	0.20	**0.61**	**0.71**	0.50	**1.00**														
Pb-F	0.51	**0.80**	**0.57**	0.51	**0.56**	0.48	**0.61**	0.41	0.34	0.45	**0.69**	0.50	**1.00**													
Mass-C	**0.64**	**0.76**	0.50	**0.83**	0.49	**0.68**	**0.82**	**0.77**	0.47	**0.75**	0.37	**0.59**	**0.67**	**1.00**												
C-C	0.52	**0.73**	0.54	**0.63**	0.52	**0.56**	**0.64**	0.42	0.40	**0.63**	**0.55**	**0.63**	**0.73**	**0.64**	**1.00**											
N-C	0.18	0.41	0.01	0.50	−0.05	0.46	0.16	0.30	0.47	0.45	0.15	**0.56**	0.15	0.33	0.22	**1.00**										
Al-C	**0.70**	0.50	0.49	0.53	**0.71**	0.40	**0.71**	**0.72**	0.34	**0.60**	0.19	0.17	0.42	**0.72**	0.28	0.10	**1.00**									
Si-C	**0.64**	0.45	0.46	0.51	**0.56**	0.41	**0.68**	**0.73**	0.26	0.49	0.12	0.14	0.39	**0.72**	0.21	0.01	**0.97**	**1.00**								
S-C	0.24	0.12	0.52	−0.08	**0.57**	−0.03	0.02	−0.11	0.03	−0.19	0.17	−0.10	0.32	−0.17	0.26	−0.22	−0.12	−0.10	**1.00**							
K-C	**0.70**	0.45	0.48	0.48	**0.61**	0.39	**0.66**	**0.74**	0.23	0.46	0.12	0.08	0.38	**0.69**	0.20	0.02	**0.97**	**0.99**	−0.06	**1.00**						
Ca-C	**0.71**	0.49	**0.66**	0.39	**0.69**	0.40	**0.76**	**0.62**	0.17	0.52	0.28	0.14	**0.56**	**0.66**	0.29	−0.10	**0.87**	**0.89**	0.10	**0.88**	**1.00**					
Ti-C	**0.69**	0.48	0.48	0.47	**0.56**	0.37	**0.63**	**0.69**	0.22	**0.56**	0.08	0.18	0.34	**0.67**	0.21	0.10	**0.95**	**0.95**	−0.19	**0.95**	**0.86**	**1.00**				
Fe-C	**0.65**	0.35	0.43	0.37	0.53	0.32	**0.62**	**0.70**	0.10	0.40	−0.02	−0.01	0.29	**0.63**	0.07	−0.03	**0.93**	**0.96**	−0.13	**0.97**	**0.89**	**0.93**	**1.00**			
Br-C	**0.60**	0.53	**0.62**	0.21	**0.67**	0.23	0.44	0.34	0.07	0.26	0.33	0.14	**0.73**	0.48	0.24	0.01	**0.57**	**0.59**	0.33	**0.61**	**0.76**	**0.55**	**0.62**	**1.00**		
Sr-C	**0.65**	0.46	0.48	**0.60**	0.50	0.50	**0.68**	**0.66**	0.34	**0.72**	0.13	0.37	0.28	**0.71**	0.25	0.23	**0.86**	**0.86**	−0.16	**0.84**	**0.79**	**0.85**	**0.84**	0.48	**1.00**	
Pb-C	**0.55**	**0.62**	**0.57**	0.16	**0.59**	0.19	0.45	0.38	0.00	0.26	0.32	0.12	**0.67**	0.51	0.25	0.00	**0.64**	**0.66**	0.19	**0.68**	**0.78**	**0.65**	**0.69**	**0.90**	0.50	**1.00**

* Coefficients >0.55 are in boldface type.

data in recent studies (Gaarenstroom *et al.*, 1977; Hopke *et al.*, 1976), but without the benefit of size-fractionated aerosol data. In the simplest form of factor analysis each *measured variable* z_j (in this case the set of coarse or fine measurements for one element) is expressed as a linear combination of m factors F_i.

$$z_j = a_{j1}F_1 + a_{j2}F_2 + \cdots a_{jm}F_m, \quad j = 1, \cdots, n > m. \tag{2}$$

The coefficients a_{jk} in Equation (2) are *factor loadings* of the variable on the corresponding factor. The factors are themselves hypothetical linear combinations of the original variables, chosen so that the correlations among the measured variables can be approximately represented by a relatively small number of factors. The actual composition of the factors is generally of less interest than the values of the loadings. The *communality* ($\leqq 1$) of a measured variable is the sum of the squares of its factor loadings.

In this work factor analysis was performed with the Statistical Analysis System (SAS) program (Barr *et al.*, 1976) using all default options including principal axis factoring without iteration, unity initial estimates of communalities, retention of all factors with eigenvalues $\geqq 1$, and orthogonal varimax rotation. The resulting four-factor solution is given in Table 6, in terms of the factor loadings and communalities for the 26 measured variables. One method for judging the adequacy of a factor analysis solution is to examine how well the solution reproduces the linear correlation matrix (Table 5). The relevant comparison is between each correlation coefficient C_{ij} and the quantity

$$S_{ij} = \sum_{k=1}^{4} a_{ik}a_{jk}. \tag{3}$$

On average the difference is about 7%. The four factors accounted for 83% of the total variance of the measured variables.

The first factor has very high loadings for coarse Al, Si, K, Ca, Ti, Fe and Sr; and medium loadings for coarse Br and Pb, and fine mass, Ca and Fe. The dominance of coarse particle crustal elements points to crustal weathering as the source of this factor. A consideration of elemental enrichment factors (Zoller *et al.*, 1974) relative to crustal abundances also supports this identification. The enrichment factors (EF) given in Table 7 were calculated from the expression:

$$\mathrm{EF} = \frac{(\text{Concentration of element}/\text{concentration of Al})_{\text{aerosol}}}{(\text{Concentration of element}/\text{concentration of Al})_{\text{crustal}}} \tag{4}$$

for each coarse and fine elemental concentration employed in the factor analysis. Aluminum was chosen as the reference because its major source is soil

Table 6. Factor analysis loading*

Variable†	Factor 1	2	3	4	Communality
Mass-F	**0.64**	0.27	**0.62**	0.03	0.88
C-F	0.29	**0.63**	0.22	**0.56**	0.85
N-F	0.38	0.20	**0.77**	0.25	0.85
Si-F	0.35	**0.86**	0.08	0.04	0.86
S-F	0.48	0.10	**0.81**	0.19	0.94
K-F	0.30	**0.78**	0.21	0.01	0.74
Ca-F	**0.60**	**0.57**	0.34	0.12	0.81
Fe-F	**0.69**	**0.51**	0.19	−0.10	0.79
Zn-F	0.08	**0.77**	0.01	0.07	0.61
Se-F	0.41	**0.79**	0.11	0.10	0.81
Br-F	−0.08	0.49	0.11	**0.67**	0.71
Sr-F	−0.04	**0.81**	−0.06	0.35	0.79
Pb-F	0.21	0.40	0.37	**0.75**	0.91
Mass-C	**0.60**	**0.65**	0.11	0.25	0.86
C-C	0.02	**0.67**	0.49	0.30	0.78
N-C	−0.02	**0.67**	−0.19	−0.03	0.49
Al-C	**0.93**	0.23	0.09	0.14	0.94
Si-C	**0.95**	0.15	0.07	0.14	0.95
S-C	−0.22	−0.17	**0.82**	0.21	0.80
K-C	**0.96**	0.11	0.12	0.13	0.96
Ca-C	**0.85**	0.08	0.28	0.33	0.92
Ti-C	**0.94**	0.17	0.04	0.12	0.93
Fe-C	**0.99**	0.00	0.06	0.09	0.99
Br-C	0.54	−0.07	0.34	**0.67**	0.86
Sr-C	**0.84**	0.37	0.04	0.02	0.84
Pb-C	**0.62**	−0.09	0.21	**0.69**	0.92
Fraction of variance	35%	24%	13%	11%	
Source	Soil	Uncertain	$(NH_4)_2SO_4$	Vehicle	

* Loadings >0.5 are in boldface type.
† F = Fine, C = Coarse.

Table 7. Aerosol enrichment factors relative to crustal abundances*

Element	Fine particles	Coarse particles	Total aerosol
Si	1.6	0.75	0.80
Al	1.0	1.0	1.0
S	1.4×10^4	97	9.7×10^2
K	4.2	0.83	1.0
Ca	3.0	2.0	2.0
Ti	2.8	1.3	1.4
Fe	3.3	0.87	1.0
Zn	5.0×10^2	11	42
As	1.6×10^4		1.0×10^3
Se	2×10^5		1×10^4
Br	6.5×10^4	1.2×10^3	5.2×10^3
Sr	12	0.8	2
Pb	5.6×10^4	6.8×10^2	4.2×10^3

* Crustal abundances from Mason (1966).

and because it has been used in this way extensively in other work. Crustal abundances were taken from Mason (1966). Enrichment factors >1 indicate an enrichment of that element relative to crustal abundances; values <1 indicate a depletion. By comparison of Tables 6 and 7, it can be seen that every coarse element having a very high loading on the first factor also has a coarse enrichment factor near 1, and vice versa. Since fine calcium and iron also have enrichment factors not greatly larger than 1, the presence of medium loadings for these components in the first factor does not appear unusual and suggests that each element has the same source for both size ranges. Coarse bromine and lead are highly enriched and undoubtedly have automotive sources. Their presence with the otherwise soil-like composition of the first factor loadings suggests a mechanism of automotive exhaust particulate deposition and subsequent resuspension. No explanation has been found for the medium loading of total fine mass on this factor.

Hopke *et al.* (1976) have noted that the concentrations of many elements found in suspended particles from coal combustion relative to Al concentrations are similar to the corresponding ratio in crustal material. Consequently the likely source of Factor 1 probably should be broadened to include coal combustion, in addition to soil suspension and roadway dust resuspension.

The second factor has high loadings of fine Si, K, Zn, Se, Sr; and medium loadings of fine C, Ca, Fe and coarse mass, C and N. This is a rather complex set of elements with no apparent single source. The set is dominated by fine components about half of which are strongly enriched (Table 7) and therefore suggestive of a complex combination of anthropogenic sources.

The loading structure of the third factor is particularly simple: high loadings of fine nitrogen, fine and coarse sulfur, and medium loading of fine mass. This set of loadings represents particulate $(NH_4)_2SO_4$, presumably formed in the oxidation and gas-to-particle conversion of SO_2 and subsequent neutralization by ammonia. The presence of fine nitrogen and sulfur on this factor is in agreement with the other results of this study involving these two elements. The presence of both fine and coarse sulfur in this factor suggests that this element has the same source in both size ranges. The medium loading of fine mass on this factor is in accordance with the earlier observation that ammonium sulfate constitutes about 40% of the total fine mass. The absence of fine carbon on this factor is contrary to the suggestion (Novakov *et al.*, 1974) that soot acts as a catalyst in the formation of atmospheric particulate sulfate. Curiously, *coarse* carbon does have an appreciable loading (0.49) on this factor, perhaps associated with incomplete combustion of coal.

The fourth factor also has a very simple loading structure. The medium loadings of fine C, Br, Pb and coarse Br and Pb indicate vehicular sources. The dominant form of lead resulting from automobile exhaust is PbBrCl (Habibi, 1973). Evidently this is the major Pb and Br source in both size ranges. Fine carbon in the form of soot is emitted in large amounts from diesel engines, while organic compounds are emitted from both diesel and non-diesel engines. Thus the presence of a medium loading of fine carbon on this factor is qualitatively consistent with vehicular sources.

SUMMARY

The principal results of this study on the composition of the Charleston, West Virginia aerosol were the following:

(1) Aerosol concentrations were obtained for total mass, carbon, nitrogen, sodium, and all elements heavier than magnesium which exceeded XRF detection limits. Separate measurements were obtained for fine and coarse size fractions of the aerosol. From the use of replicate samplers average precisions of 5 and 15% were found for total fine and coarse mass measurements, respectively. Corresponding average precisions for elemental components were 11 and 23%.

(2) Elements were generally found predominantly in one size fraction or the other. Carbon was the only major element that was about equally distributed between the two.

(3) Fine nitrogen was virtually all in the form of NH_4^+, with fine nitrogen as NO_3^- measuring only about 1% on average. Fine sulfur was virtually all in the form of SO_4^{2-}. The amounts of NH_4^+ and SO_4^{2-} were stoichiometrically consistent with the chemical form $(NH_4)_2SO_4$ for the fine fraction.

(4) On average, 65% of the total aerosol mass can be identified with known or likely chemical compounds. Whatever contribution water may make to the unidentified portion of the measured mass, it must be as a stably bound form, such as water of hydration.

(5) Interrelationships between the measured elements were examined through linear correlation coefficients and factor analysis. The latter showed that

only four sources were needed to account for 83% of the variance in the data set. The sources were crustal material likely from soil and/or coal ash, ammonium sulfate presumably from gas-to-particle conversion of SO_2, automotive exhaust, and a fourth source of uncertain anthropogenic origin.

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